CONTROL OF ACID MINE DRAINAGE BY APPLICATION OF BACTERICIDAL MATERIALS

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INTRODUCTION

The kinetics of acid formation are dependent on the availability of oxygen, the surface area of pyrite exposed, the activity of iron-oxidizing bacteria, and the chemical characteristics of the influent water. The principal iron-oxidizing bacterium involved in accelerating pyrite oxidation is Thiobacillus ferrooxidans (9, 15).[4] The Bureau of Mines has previously reported the results of full-scale field tests that showed how anionic surfactants (cleansing detergents) can be used to reduce the activity of T. ferrooxidans (12-13) and thereby abate acid formation. After a brief discussion of the literature, this paper will review the surfactant solution technique and report progress on two alternative procedures.

ACKNOWLEDGMENTS

The controlled release surfactant formulations were provided by BFGoodrich and Granger Technologies, Inc. The assistance of both companies is gratefully acknowledged.

BACKGROUND INFORMATION

The possible involvement of bacteria in the formation of acid drainage was first reported in 1919 by Parr and Powell, who determined that coal inoculated with an unsterilized ferrous sulfate solution produced drainage with higher concentrations of sulfate than did sterile controls (16). The possibility of reducing acid drainage by bacterial inhibition was first considered in 1953 but was rejected as impractical due to probable rapid repopulation (14). Later laboratory studies demonstrated the vulnerability of T. ferrooxidans in coal and coal refuse to anionic surfactants and consequent acidity reductions of 65 to 80 pct (7).

Full-scale tests at active and inactive coal refuse areas demonstrated that sodium lauryl sulfate (SLS) surfactant application could effectively reduce acid production and thereby lower water treatment costs. Sufficient surfactant was applied by hydroseeder to the coal refuse to saturate the adsorptive capacity of the top 1 ft of refuse, based on a laboratory determination (13). The 1-ft-thick treatment zone was selected for several reasons: (1) Oxidation was assumed to occur largely in a near-surface oxygenated zone (3, 6), (2) desorption and downward migration would result in treatment at greater depth, and (3) it was preferred to undertreat rather than overtreat, to prevent significant surfactant concentrations off the site.

Water quality improved at the test sites in 1 to 3 months. Acidity, sulfate, and manganese decreased 60 to 90 pct; iron decreased 90 to 95 pct (fig. 1). After about 4 months, contaminant concentrations slowly climbed back to

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[4] Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

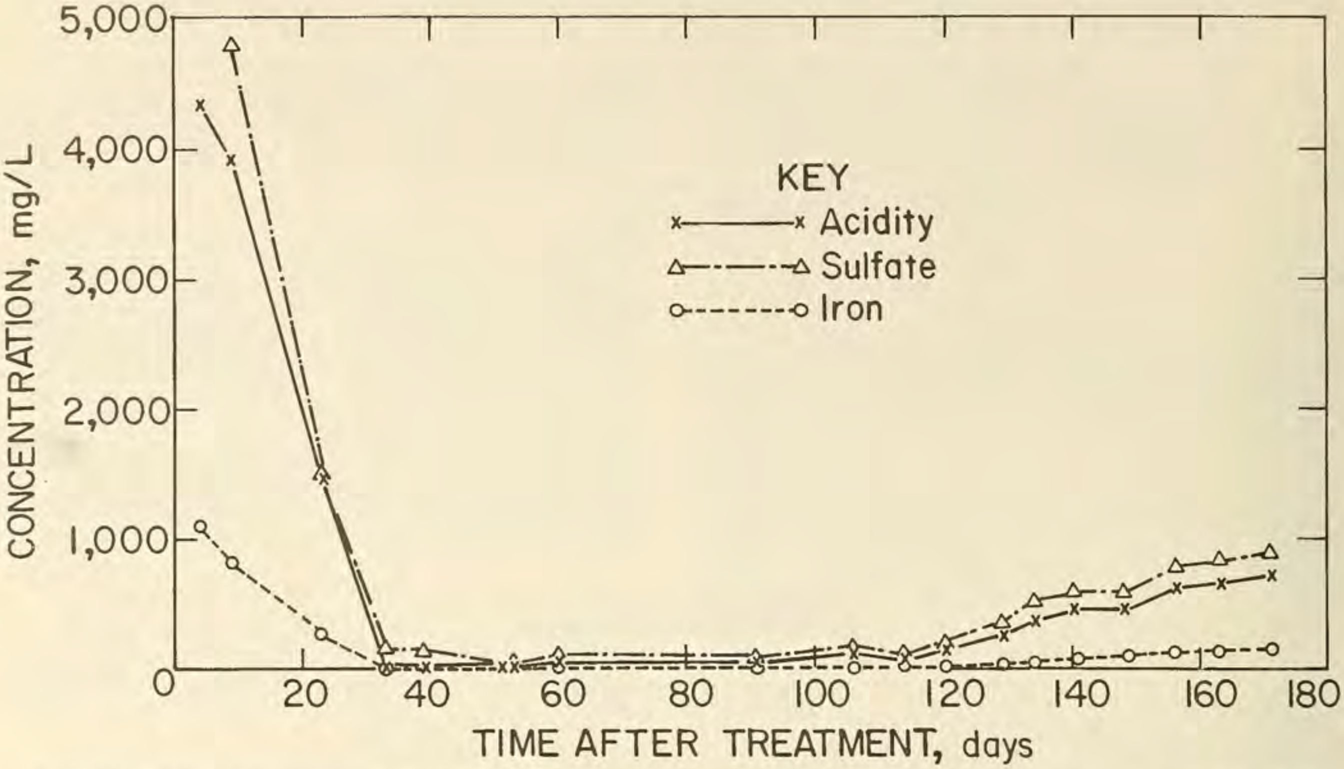

FIGURE 1. - Improvement in drainage quality following surfactant solution application at a site in West Virginia.

previous levels. Effluent surfactant concentrations were negligible.

As a result of these tests, the mining industry has begun to apply surfactants to coal refuse, coal stockpile areas, unreclaimed mine spoil, and waste sulfide rock, with mixed results. One coal company that applied an anionic surfactant two or three times a year to a developing coal refuse pile has had no acid problem over a 5-yr period despite the fact that coal refuse at the plant typically produces acidic drainage within 6 months. At the other extreme are sites where the technique produced no apparent effect or only a short-term improvement in water quality. Some of these failures can be explained simply, such as when the dosage rate or site conditions were obviously inappropriate. At other sites it may never be known why the technique failed to reduce acid production.

A previous report describes in some detail when and how the surfactant should be applied (13). It is worthwhile to restate the three most significant points:

1. Determine beforehand if the technique is potentially cost effective for the site. Assume a material cost of $600/acre annually plus the cost of three applications by watering truck or hydroseeder, a 60-pct decrease in neutralization costs, and a 90-pct decrease in sludge accumulation; if the calculated annual savings are not significantly greater than the assumed costs, the technique is probably not appropriate.

2. The surfactant must reach and adsorb to the pyritic material. If the site is covered with topsoil, a surfactant application will not reach the pyritic material and will therefore accomplish nothing. If an adsorption test indicates that the pyritic material has low adsorptive capacity, the surfactant will wash away rapidly, providing only brief abatement.

3. Owing to slow hydrologic flow-through time or pooled acid water on the old mine floor or in a refuse area, the effect of surfactant treatment may be delayed, masked, or made insignificant. In the case of slow flow-through time (as much as a year at some sites), improvement in water quality at the discharge point cannot occur faster than water flows through the material. If a significant pool of acid water exists, years of continued application of surfactant could be required before an increase in water quality is observed, unless the acid pool is first neutralized or drained.

Application of anionic surfactant solution, although effective in reducing water treatment costs, cannot be regarded as a long-term control measure. Two modifications of the basic approach are being considered by the Bureau of Mines:

1. The surfactant can be rendered less soluble. This has been accomplished using slow-release technology developed for more conventional biocides (2, 10). Controlled release of surfactant over a period of many years may be possible.

2. Other environmentally safe chemicals have been identified that inhibit T. ferrooxidans and that react with acid mine drainage to form slightly soluble precipitates. Thus, these chemicals may form their own slow-release material in the acid-producing environment.

The remainder of this paper will summarize the results of laboratory and pilot-scale experiments and introduce full-scale field tests that are in progress.

SLOW RELEASE OF SURFACTANTS

This approach has been under investigation since surfactants were first considered for field use (7). Early surfactant-rubber formulations reduced acid formation by over 95 pct in a pilot-scale field test but were effective for less than 1 yr (8). Subsequent research has been directed towards extending the release lifetime of the material and field tests of the resultant formulations.

LABORATORY TESTS

Laboratory and pilot-scale tests have been conducted on more than 20 materials manufactured for the tests by BFGoodrich and Granger Technologies. The materials, manufactured prior to 1982, all contained SLS as the active ingredient. The compositions are proprietary, and materials are referred to in this report by alphabetic code.

Laboratory tests were conducted initially to determine which variables most strongly influenced the SLS release rates (11). Every parameter investigated, including nature of matrix, SLS loading, and surface area, influenced the rate of dissolution.

Figure 2 shows release curves for five formulations for illustrative purpose. The data were obtained by periodically rinsing a 5-g sample with 100 mL deionized water. Leachates were combined to 400 to 500 mL total volumes and analyzed for anionic surfactants by the methylene blue method (1). The percent SLS remaining in the matrix was calculated from the nominal SLS content of the sample and the cumulative mass of SLS extracted. Nominal SLS contents, ranging from 20 to 65 pct of the total sample weight, were normalized to 100 pct for comparison.

All formulations exhibited an initial rapid release of detergent followed by a slower dissolution phase. The first phase was more pronounced in samples having a larger fraction of SLS at or near the pellet surface. For example, samples D and E are cylindrical pellets of the same formulation having diameters of 4.6 and 3.2 mm, respectively. Approximately three times more detergent was dissolved

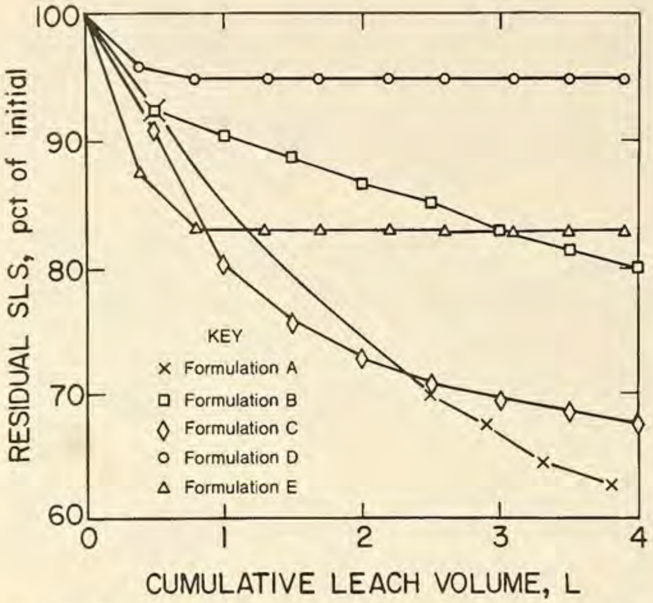

FIGURE 2.-SLS release curves for five controlled-release formulations subjected to intermittent leaching in the laboratory.

from sample E than from sample D in the first liter of leach water (fig. 2).

Under the experimental conditions 4,000 mL is approximately equivalent to 40 in of precipitation. Cumulative extracted SLS at this point ranged from 4 to 38 pct of the total surfactant content of the samples. These values cannot be extrapolated to an expected lifetime, however, because release rates were decreasing over time. In some formulations much of the detergent appeared to be unavailable (curves D and E of figure 2).

While the laboratory results confirmed that surfactant loading, pellet geometry, and matrix type affected SLS release rates, no empirical equations could be developed to predict release curves for new formulations. Outdoor evaluation of potential materials was considered preferable to continued laboratory testing.

PILOT-SCALE TESTS

Pilot-scale testing was conducted outdoors to determine release rates under field conditions. The test area consisted of two small coal refuse piles, each about 7 ft wide, 12 ft long, and 1.5 ft high at the lengthwise crest. Garden edging was used to divide each slope into six test plots. A rain gage was placed about 15 ft from the refuse piles.

Approximately 250 to 500 g of pellets were spread by hand on each of 21 test plots during February 1983. The coal refuse contained about 5 pct sulfur and produced drainage acidity on the order of 10^4 mg/L prior to the controlled release application. No attempts were made to monitor drainage quality during the experiment.

Periodically, a selected number of pellets were removed at random from each plot and residual SLS content was determined. In one method, the samples were dried to constant weight at room temperature, and SLS release was calculated by weight loss:

SLS release = nominal weight

- actual weight

This method is based on the assumption that all weight loss resulted from SLS dissolution. Nominal weights were determined as the mean weight of 10 replicate samples of fresh pellets of the same formulation.

The second method involved aqueous extraction of residual SLS from air-dried samples. The pellets were placed in a minimum of 500 mL deionized water and allowed to equilibrate for several days. The extracts were analyzed for anionic surfactants, and the extracted pellets were air-dried for determination of matrix weight. This method was based on the assumption that all residual SLS could be extracted into deionized water. Values were calculated from actual dry matrix weight and nominal dry matrix weight. A typical release curve is shown in figure 3 for a formulation nominally containing 50 pct SLS by weight. Three calculation methods used to determine residual SLS content usually yielded results that agreed to within 10 pct. This

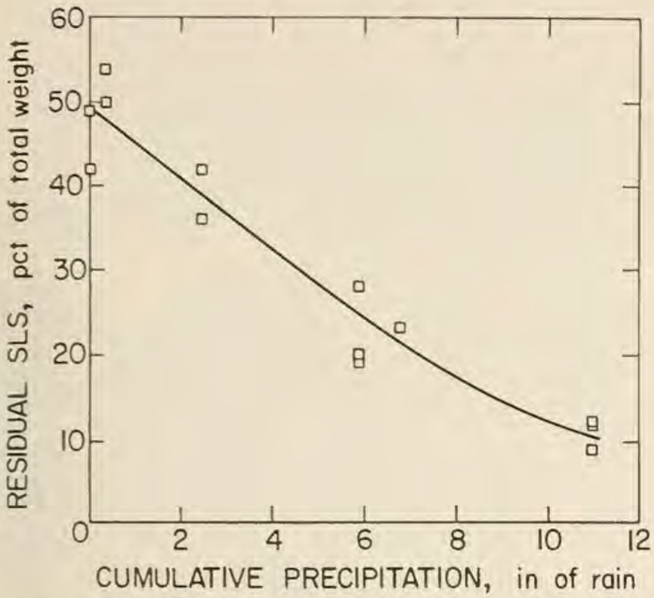

FIGURE 3. - SLS release curve from the outdoor pilot-scale test. Formulation was approximately 50 wt pct SLS. Multiple data points were calculated using weight loss and extraction data.

TABLE 1. - Residual SLS after exposure of formulations to 11 in of precipitation on coal refuse test piles

Plot No	SLS content, pct of initial[1]	Plot No	SLS content, pct of initial[1]
1...	-2	12...	-15
2...	12	13...	18
3...	27	14...	20
4...	-14	15...	-7
5...	0	16...	98
6...	-16	17...	65
7...	-8	18...	20
8...	-5	19...	47
9...	16	20...	125
10...	-18	21...	83
11...	90		

[1] Initial SLS content, ranging from 20 to 65 pct, was normalized to 100 pct.

large variation is due to the indirect measurements mentioned previously. The curves generally followed the same pattern observed in the laboratory study (fig. 2), although SLS release was much more rapid in the field.

Table 1 shows the residual SLS content for all the formulations after 11 in of precipitation. Essentially all the surfactant dissolved from nine of the samples within the 4-month period represented by the tabulated results. Seven of these samples were composed of early matrix formulations. At the other extreme, two samples released essentially none of the surfactant during the pilot-scale test. Several formulations exhibited release rates (residual SLS 65 to 90 pct) that might provide the desired release lifetime of several years.

Negative numbers on table 1 resulted when some of the weight loss assumed to be SLS dissolution was actually loss of matrix. Some of the thinner rubber matrices underwent significant degradation that produced visible shrinkage of the pellets. All samples tested in the laboratory and in the pilot-scale test exhibited much higher SLS dissolution rates in the latter case. Exposure to ultraviolet light and moist, acidic refuse probably contributed to faster release through degradation of the matrices. Burial of the controlled release pellets beneath a soil cover should retard release rates by reducing degradation and limiting contact with rainfall.

FIELD PROJECTS

The Bureau is participating in one field trial of the controlled release concept (5). The site is a 15-acre isolated ridge in Upshur County, WV, which was mined and reclaimed in three sections. State-of-the-art reclamation techniques, including a clay cap emplaced over the toxic material, were used (19). Surfactant solution and a controlled release surfactant formulation were applied to one section below the clay layer. Since completion of reclamation during spring 1983, seeps and surface runoff have been monitored. To date, the postmining hydrology has not developed sufficiently to allow characterization of drainage quality from the various sections.

Selection of the controlled release material was based on early laboratory data; we now know that the surfactant is released from the matrix in less than 1 yr when the pellets are applied to the surface of acidic material. Exposed to no sunlight and less water under the clay cap, detergent release should be significantly slowed.

Both Goodrich and Granger are now developing new formulations to optimize surfactant release rates. The former company is currently conducting field tests of 1984 formulations that we have not tested (4). In the oldest test, the controlled release pellets were applied during summer to a portion of a coal refuse site prior to application of seed and soil to the entire site. At the end of the first growing season, there was good vegetation cover on the treated refuse, compared with extensive acid burnout areas on the untreated portion.

ORGANIC ACID INHIBITORS

We began to investigate another alternative for control of T. ferrooxidans when the limitations of the solution surfactant technique became apparent. For materials having low affinity for surfactant and sites having high water flow rates, a less soluble inhibitor was needed. The concept was to identify organic compounds with the following properties:

1. Toxic to T. ferrooxidans but innocuous to other organisms.

2. Sparingly soluble in AMD or neutralized mine drainage.

3. Actively bactericidal once redissolved or in response to acid production.

Preliminary experiments consisted of a survey of 25 organic compounds, which might be inhibitors and which might precipitate as sparingly soluble compounds in AMD. These experiments yielded two candidate compounds: sodium benzoate and potassium sorbate. We found that 0.1-pct solutions of either salt formed organic precipitates when added to synthetic AMD in the pH range of 4 to 5. The precipitates probably consist of ferric or ferrous salts of the organic acids. Further testing was encouraged by the fact that these organic acids are used as food and beverage preservatives and hence should be environmentally safe.

Laboratory tests of bacterial inhibition have previously been reported (18). In solution cultures of a pure strain of T. ferrooxidans, bacterial activity was monitored as the utilization of ferrous iron in the medium. The bacteria derive energy from oxidation of ferrous iron. Figure 4 illustrates the results in uninhibited bacteria culture, in sterile medium, and in two bacterial cultures containing benzoic acid. We found that 10 mg/L of either benzoic or sorbic acid was sufficient to decrease the rate of ferrous iron oxidation to that of sterile controls.

PILOT-SCALE TESTS

Bactericidal effectiveness of potassium sorbate, sodium benzoate, and SLS was investigated for reducing acid production from fresh and weathered refuse;

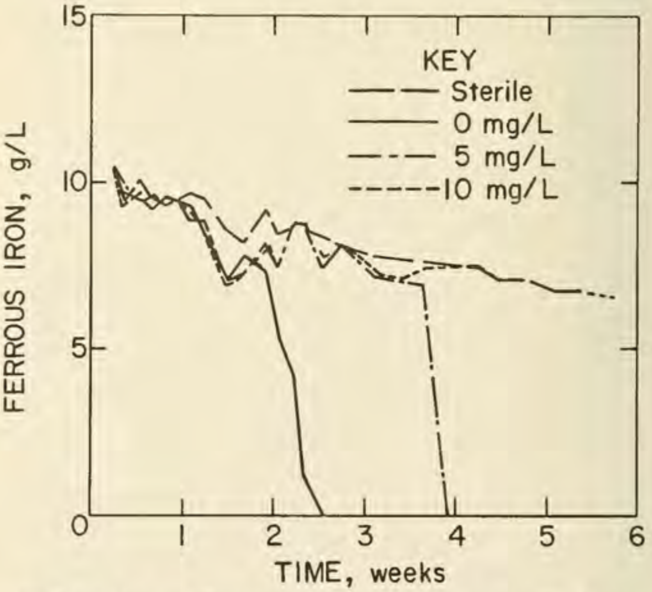

FIGURE 4. - Ferrous iron oxidation by T. ferrooxidans, as a function of added benzoic acid. The sterile culture indicates the rate of abiotic oxidation.

preliminary results have been published previously (17).

Drums filled with 200 kg of fresh coal refuse were leached weekly by saturating the material for 24 h with tap water. The drained leachate was analyzed for pH, acidity, total dissolved iron, and sulfate. In the first week of the experiment, 24 L of inhibitor solution replaced the water in six of the drums. The three inhibitors were each tested at concentrations of 500 and 5,000 mg/L (equivalent to 60 and 600 mg chemical per kilogram of refuse). Ten drums of refuse were "treated" with tap water and used for experimental control.

The low doses of treatment chemicals were marginally effective, delaying acid production 1.5 to 5 weeks after leachate from the control barrels became acidic (fig. 5). High treatment doses of 5,000 mg/L were effective for 8 to 10 weeks (fig. 6). Potassium sorbate yielded the best results in both treatment series.

At low dosage rate, sorbate was least expensive on the basis of cost per week of delayed acidification. However, at the high dosage rate, the duration of the treatments were more similar and the chemical of choice would probably depend on cost per pound. Approximate bulk prices are \$0.90/lb for sodium benzoate, \$1.67/lb for SLS, and \$3.52/lb for potassium sorbate. Field trials will be required before an accurate cost analysis can be made. The longevity of SLS treatment under field conditions is about twice as great as in the high-dosage pilot-scale test; the experimental conditions of extremely high leaching rates probably underestimate the duration of all three inhibitors.

After 22 weeks of weathering, 9 of the 10 control barrels were treated with the chemical inhibitors to determine their effectiveness in the highly acidic environment of aged refuse. Drainage acidity levels were approximately 8,000 to 14,000 mg/L at the start of this experiment. During the 22-week leaching program, drainage from the untreated barrel retained as a control became 70 pct less contaminated. The easily oxidizable pyrite may have been consumed during the initial 22 weeks of weathering; cumulative sulfate load data indicated approximately 10 pct of the total pyrite had been oxidized before treatments were applied to the aged refuse.

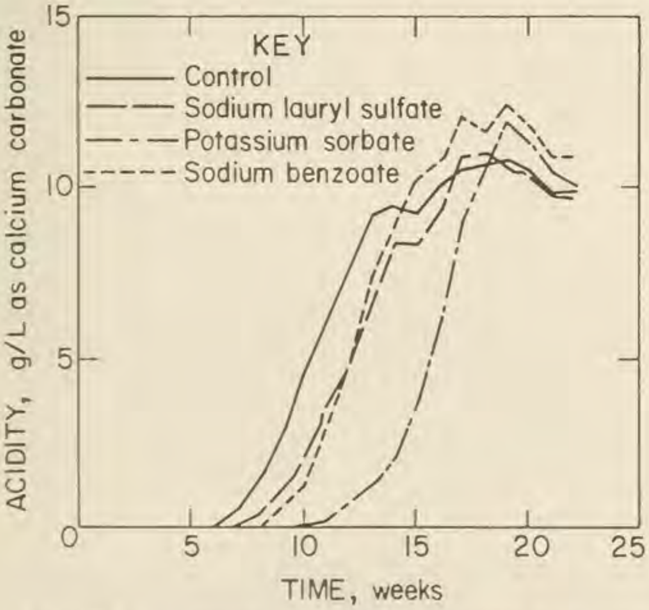

FIGURE 5. - Acidity levels in leachate from coal refuse treated with 500 mg/L of chemical inhibitor.

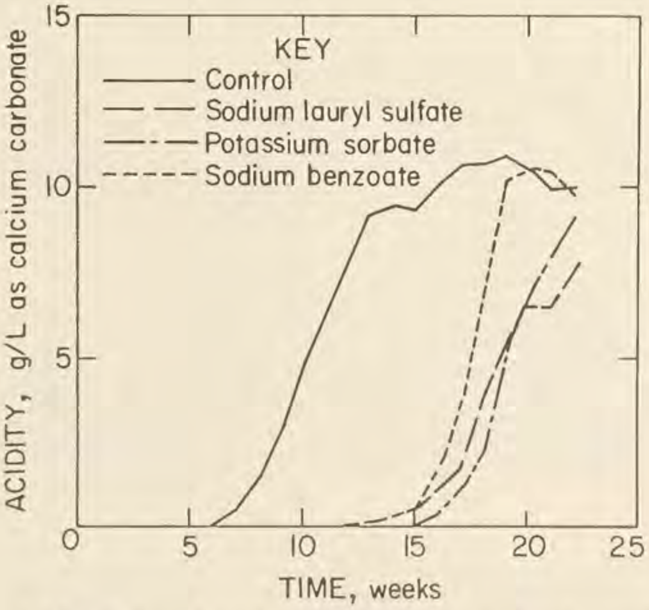

FIGURE 6. - Leachate acidity from fresh coal refuse treated with 5,000 mg/L of chemical inhibitor.

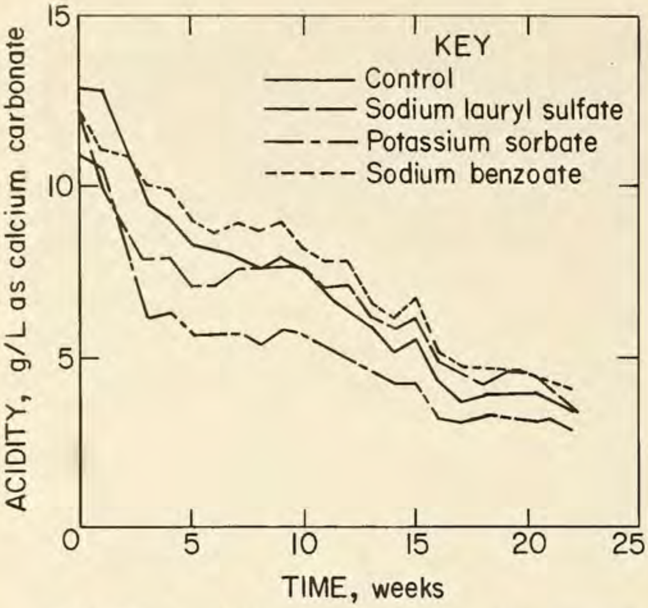

FIGURE 7. - Effect of low doses of treatment chemicals on weathered coal refuse leachate compared with leachate from untreated refuse.

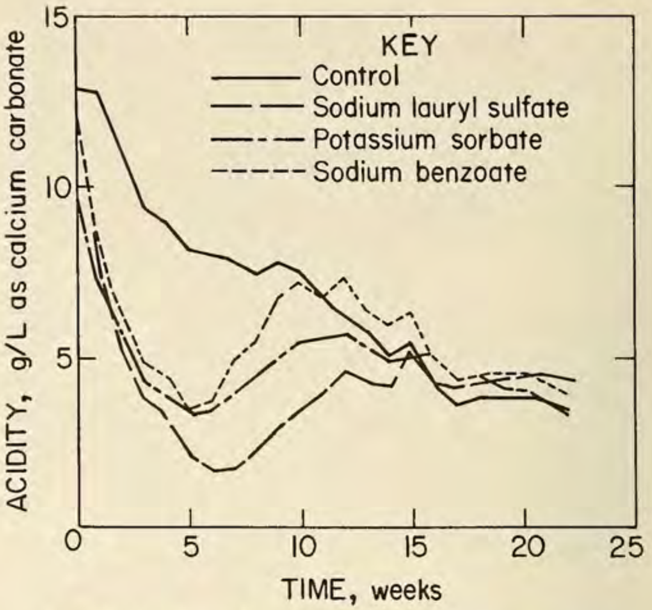

FIGURE 8. - High doses of three treatment chemicals reduced acidity of weathered coal refuse leachate, compared to leachate of untreated coal refuse.

Superimposed on the trend of decreasing contaminant concentrations, additional improvements in drainage quality were observed (figs. 7-8). At the low dosage rate of 500 mg/L, only potassium sorbate produced significantly better drainage than did the control. All three chemicals were effective at the 5,000-mg/L dosage rate. Cumulative acid loads (fig. 9) were 17, 29, and 38 pct lower for sodium benzoate, potassium sorbate, and SLS treatments, respectively, at the end of 22 weeks than in the control drainage. Seven weeks after treatment, when the inhibitors were most effective, cumulative acid loads were 45 to 62 pct lower in the high treatment dose leachates than in the control leachate.

A field test is now in progress at a revegetated mine site in West Virginia. Dry potassium benzoate powder was applied to the surface on 2 acres overlying the major acid-producing zone. Water quality is being monitored in the vadose zone, in the saturated zone, and at the discharge seep.

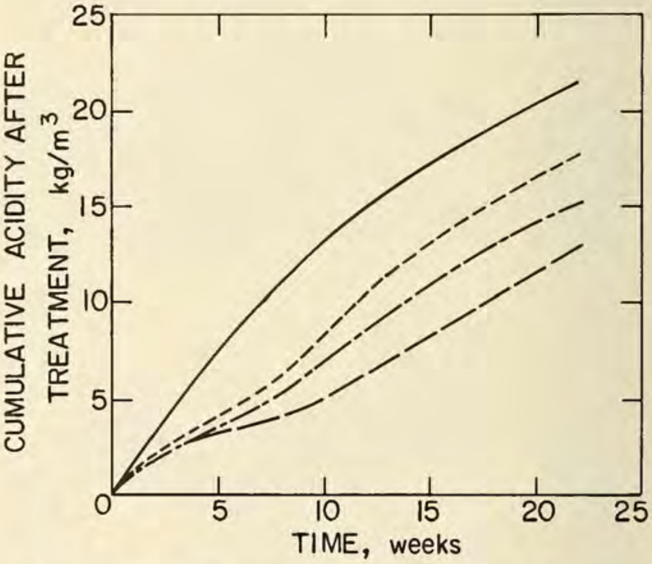

FIGURE 9. - Cumulative acidity produced by weathered coal refuse after application of high doses of inhibitory chemicals. Curve symbols as in figure 8.

SUMMARY

Preliminary experiments were conducted on two alternatives to the surfactant solution technique for controlling acid drainage. Controlled release of surfactants appears to be a feasible means of extending the bactericide lifetime.

Further work, in the form of field tests, is needed to determine the cost effectiveness of this method.

The organic inhibitors, benzoate and sorbate, were of the same general order of effectiveness as surfactant solution in pilot-scale tests. There may be some cost advantage in using benzoate; a field test of this compound is in progress. Under moderately acidic conditions where adsorption is unlikely, such as in some underground mines, the metal-organic salt precipitate may have further advantages in extending the duration of acid control.

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By Staff, Bureau of Mines

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